

APPROACHES TO NEW ENDCAPS FOR IMPROVED OXIDATION RESISTANCE

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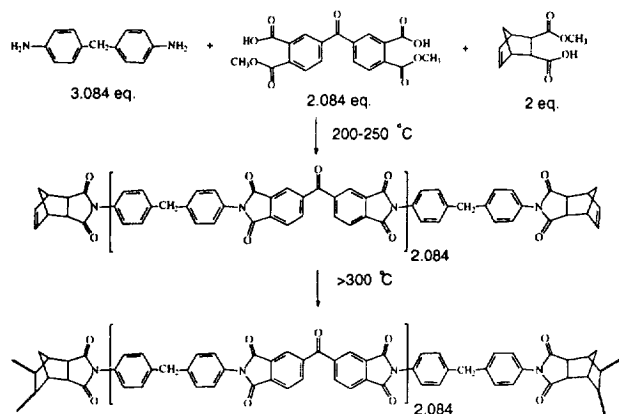
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Introduction

Norbornenyl-end capped PMR polyimide resins¹ are widely used as polymer matrix composite materials for aircraft engine applications,² since they combine ease of processing with good oxidative stability up to 300 °C. PMR resins are prepared by a two-step approach involving the initial formation of oligomeric pre-polymers capped at both ends by a latent reactive end cap. The end cap undergoes cross-linking during higher temperature processing, producing the desired low density, high specific strength materials, as shown (Scheme 1) for PMR-15.³



Scheme 1

The end cap facilitates processing by controlling the molecular weight of the oligomer and allowing flow before it cross-links. However, after cross-linking, this very end cap accounts for much of the weight loss in the polymer on aging in air at elevated temperatures.⁴ Understanding this degradation provides clues for designing new end caps to slow down degradation, and prolong the lifetime of the material.

Previously⁴, we reported studies on the thermo-oxidative aging of a modification of PMR-15, in which we ¹³C labeled the end cap at the methyne carbon α to the carbonyl groups. This labeled carbon in the as-processed polymer has an enhanced ¹³C NMR peak at 48 ppm (Figure 1a). The solid NMR difference spectrum of the ¹³C labeled PMR-15 aged as a powder for up to 64 hours indicates that, upon oxidation, nearly all of the nadic peak is consumed (Figure 1b). In its place, three broad peaks for ¹³C labeled carbons grew in at 105-120, 125-140 and 150-165 ppm. Based on these chemical shifts, results from delayed decoupling NMR experiments, and comparison to model compounds⁵, we can conclude that the major non-volatile products of oxidation are as shown in Scheme 2, and that this oxidation proceeds through two primary pathways.

Path A degradation is proposed to proceed through initial opening of the norbornyl ring to form a biradical which undergoes attack of oxidation to form a 2-hydroxy substituted maleimide **2**. Structures like maleimide **2** can account for the peaks at 105-120 and 150-165 formed on oxidation of labeled polymer. Path B degradation proceeds through oxidation of the bridging methylene of the norbornene moieties followed by carbon monoxide extrusion. Aromatization of the resulting biradical ultimately leads to substituted phthalimide **4** or quinone **3**, and related secondary degradation products. Structures such as these account for the large peak at 125-140 ppm which grows in the spectrum of the labeled polymer after oxidation.

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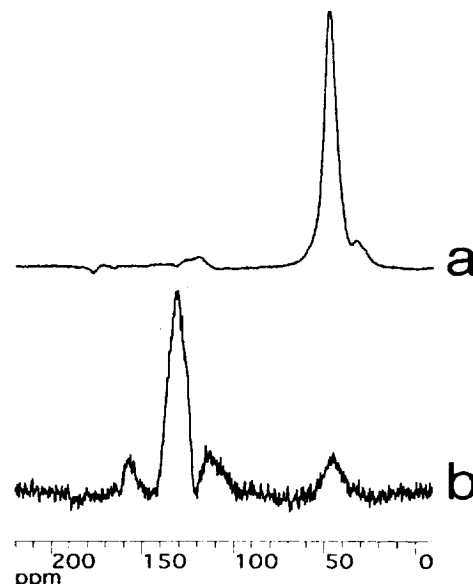
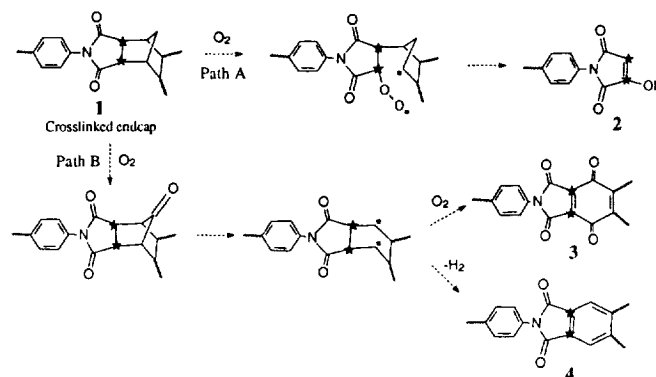
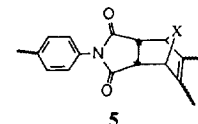


Figure 1. Difference spectrum of ¹³C-labeled carbon on endcap a) before and b) after aging in air at 300 °C as powder for 64 hours.



Scheme 2 (★=labeled carbons)

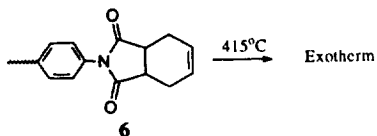
Path A oxidation products like **2** are cleavage products that are most likely formed concomitant with large amounts of weight loss in the polymer system. In contrast, structures like **3** and **4** from path B are formed with very little weight loss. Therefore, new end cap structures that more strongly favor path B degradation should lead to lower weight loss in addition polyimides, and result in less shrinkage and cracking in the oxidation layer.⁶ In this paper, we wish to explore the design of new end caps which might favor path B degradation. We propose to utilize structures like **5** below where



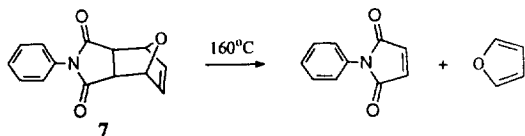
X is more labile or more easily oxidized to a more labile group under aging conditions. Such a structure should aromatize more easily to stable structures like **3** and **4**. It is important, however, to preserve the desirable processing properties of the norbornene end cap. Hence, X must also be stable enough to survive imidization (200 °C) and cross-linking (315 °C). In addition, cross-linking must occur in the same way as for the parent norbornene structures (mostly through the double bond, and not mostly through retro-Diels-Alder reaction) or oxidation will also proceed a different way.

In short, our theory is that using a more labile X group than the methylene in the parent norbornenyl-end cap could actually improve oxidative stability. Hence, one must first consider 1,2,3,6-tetrahydrophthalimide as an end cap that contains no X group at all. This structure was tried by St. Clair and St.

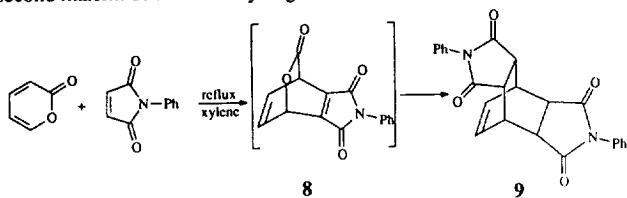
Clair⁷ as an end cap for polyimide adhesives. However, there is no evidence of cross-linking in this system until 415 °C. If the cross-linking temperature could be lowered—either by substitution on the ring or by catalysis—this might be a viable replacement for the norbornene end cap. Indeed, onset of decomposition for polymers made with this end cap was shown to be at a higher temperature than for the norbornenyl-end cap.



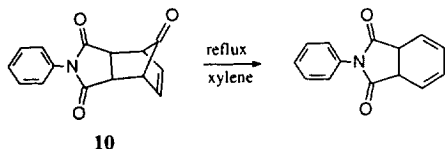
The oxygen-bridged analogue, 7, (X=O) of the norbornenyl-end cap⁸, and by extension, nitrogen and sulfur bridged analogues⁹ are also not suitable candidates. Since furan, pyrrole and thiophene are all highly aromatic, these structures favor retro-Diels-Alder reaction over cross-linking through the double bond. Therefore, this would not give the same type of cross-linked structure that could subsequently be aromatized via path B.



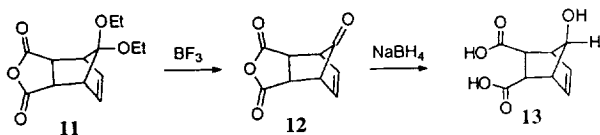
The carboxy-bridged analogue of the norbornenyl-endcap, with X=CO₂, is also not a suitable replacement. The CO₂ group is readily lost at 140 °C. The desired structure, 8, cannot even be isolated in a Diels-Alder reaction between 2H-pyranone and maleimide. The molecule so easily loses the CO₂ bridge that a second maleimide adds readily to give bis-adduct 9.



For the same reason, an oxonorbornene structure, 10, (X=CO) would not be a suitable replacement candidate for the norbornenyl-end cap. As shown below, the carbonyl bridge is too labile to survive imidization, since loss of CO occurs readily at temperatures as low as 140 °C.¹⁰ On the other hand, this substitution on the bridge gives us entrée into a host of other substituted norbornenyl endcaps which may be suitable candidates.



For example, norbornen-7-one-2,3-dicarboxylic acid anhydride, 12, was synthesized from the diethyl ketal, 11 by the method of Fuchs¹⁰. Reduction of the carbonyl of 12, with sodium borohydride gives the 7-hydroxynorbornene-2,3-dicarboxylic acid, 13, in near quantitative yield. This structure is of interest because in a polymer, the hydroxy-bearing carbon should more easily oxidize to carbonyl on aging than the methylene in the parent norbornenyl-end cap. Therefore, 13, used as an end cap should more highly favor path B degradation.



The 7-hydroxydiacid 13, was used in place of the norbornenyl-endcap to synthesize polyimide molding powder. Analogous to that shown in Scheme 1, the molding powders were synthesized with a formulated molecular weight of 1500 from benzophenone-3,4,3',4'-tetracarboxylic dianhydride (BTDA) and 4,4'-methylenedianiline (MDA). The three monomers were combined by grinding the solids together and heating the mixture for 1.5 hours at 200 °C.

Solid CP-MAS NMR of molding powder made from 13 has nine peaks: δ 43.6, 48.8, 87.6, 125.4, 130.0, 141.2, 166.5, 177.4, 193.2. The peak at 87.6 is assigned to the carbon bearing the hydroxy group. All other peaks correspond to those of PMR-15 molding powder.

Differential scanning calorimetry (DSC) of molding powders made from both the parent endcap (PMR-15) and 13 shows the broad exotherm usually associated with the crosslinking (Figure 2) in the norbornenyl system. However, the exotherm for the molding powder made with 13 occurs approximately 50 °C lower than that for PMR-15, not unlike other substituted endcaps previously studied¹¹. Nevertheless, the exotherm is high enough for the new endcap to survive intact through imidization without crosslinking.

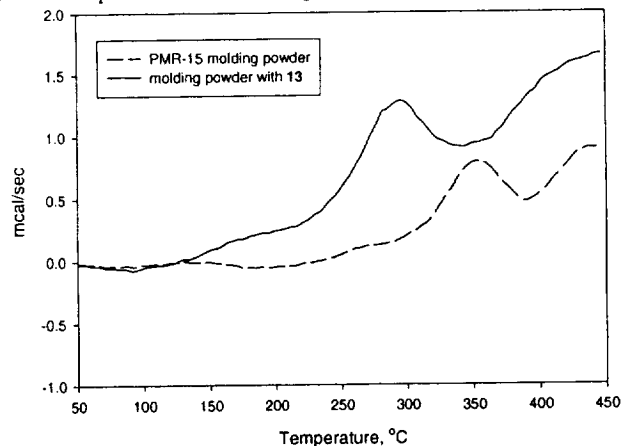


Figure 2. Comparison of DSC of molding powders of PMR-15 and the corresponding polyimide endcapped with 13.

Conclusions

Possible replacement end caps are considered that should favor path B degradation and lead to lower weight loss in the resin system. Preliminary evaluation demonstrates that molding powder made with 7-hydroxynorbornene-2,3-dicarboxylic acid, 13, as the end cap can be fully imidized at 200 °C. By DSC, onset of cross-linking occurs approximately 50 °C lower than for the unsubstituted end cap.

The hydroxy-bearing carbon on 13 should be more easily oxidized to carbonyl on aging in the polymer than the parent end cap. Therefore, the new end cap should more highly favor path B degradation. However, processing studies, long term weight loss, and careful evaluation of degradation mechanisms must be carried out to fully assess 13 as a more thermo-oxidatively stable replacement for the parent norbornenyl-end cap.

Acknowledgement. The authors would like to thank Mr. Daniel Scheiman of DYNACS Engineering for performing thermal analysis and infrared spectroscopy.

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